

### Biological Metal Clusters: Biophysical and Model Studies (3)

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Superoxide dismutases (SODs) are metalloenzymes that catalyze the disproportionation of superoxide radical anion. As such, SODs are important components of systems that protect biological molecules from oxidative damage by superoxide or reactive oxygen species derived from superoxide. Examples of enzymes containing Cu, Mn and Fe as the redox-active metal have been characterized. Recently, a SOD containing one Ni atom per subunit was reported by a Korean group (Kang, *et al.*). The amino acid sequence of the NiSOD deduced from the nucleotide sequence of the structural gene has no homology with other SODs. Ni K-edge XAS was used to show that the oxidized (epr active as isolated) enzyme has five-coordinate Ni centers composed of three S-donor ligands, one N (identified as such from epr hyperfine) and one other O/N-donor ligand, despite the known reactivity of Ni thiolates with oxygen and peroxide (the products of the reaction). Upon reduction with dithionite, the Ni site adopts a four-coordinate planar geometry with the loss of one O/N-donor ligand. These studies have been reported (Choudhury, S.B., Lee, J.-W., Davidson, G., Yim, Y.-I., Bose, K., Sharma, M.L., Kang, S.-O., Cabelli, D.E., Maroney, M.J. *Biochemistry* 38: 3744-3752, 1999). Recent kinetic studies suggest that the reduced enzyme prepared by reduction with dithionite, peroxide, or by irradiation are catalytically viable but show no spectral evidence of producing the resting, oxidized state. Each of these reduced forms is being studied by Ni K-edge XAS and preliminary results show that each structure is distinct.